

LOW TEMPERATURE CLEAVAGE REACTIONS OF ILLINOIS NO. 6 COAL

Frank R. Mayo, David H. Buchanan,¹ and Lee A. Pavelka

SRI International, Menlo Park, California 94025

This paper presents a progress report on our efforts to determine the kinds and proportions of single bond in Illinois No. 6 coal that can be broken below 100°C. The principal obstacle to the use of present liquefaction processes is the high cost of plants that would employ the required high temperatures and pressures. Our work deals only with low-temperature processes near atmospheric pressure. It has focused on (1) the asphaltol fraction of Illinois No. 6 coal, which is the pyridine-soluble, toluene-insoluble fraction that comprises about two-thirds of the 15% of coal that can be extracted by pyridine, and (2) the pyridine-extracted coal, which is about 85% of the initial dry coal, and which represents the essence of the liquefaction problem.

Oxidations

Previous work by Huntington et al² described the effects on the same two substrates of (1) AIBN-initiated oxidations in pyridine solution at 50°C, and (2) refluxing with alcoholic KOH (78°) without oxygen. Either reagent would reduce the number-average molecular weight (\bar{M}_n , by vapor-phase osmometry) of the asphaltol by nearly 50% but sequential treatment with both reagents produced little additional effect, as if the two reagents were affecting similar bonds. Only about 10% of the extracted coal was made soluble in pyridine, but some substrate became soluble in alcoholic KOH.

NaOCl oxidation of very finely divided extracted coal in water suspension at 30° and pH 13 has been much more effective in dissolving this material.³ 76% of the carbon in the extracted coal has been converted to black acids (\bar{M}_n about 1000) soluble in aqueous base, and 7% to water-soluble acids; 4% of the initial carbon was undissolved; the remaining 12% is presumably in carbon oxides. Oxygen oxidation of extracted coal in water suspension at pH 13 and 50° is much slower but has led to 85% dissolution of the coal and recovery of 66% of the original coal in black acids. Oxidations of asphaltol, well dispersed in water at pH 13, gave better results: with NaOCl at 30°, 99% dissolution and 93% of the carbon in black acids; with oxygen at 50°, 98% dissolution and 80% of the carbon in black acids.

These oxidations in water suspension at pH 13 and oxidations with AIBN and oxygen in pyridine solution² at 50°C appear to proceed by different mechanisms. In radical-initiated oxidations of extracted coal, the H/C ratio decreases from .73 to .69, as if benzylic hydrogen were being removed preferentially. However, in both NaOCl and oxygen oxidations of both asphaltol and extracted coal in water, H/C increases somewhat, notwithstanding replacement of some H by O, suggesting preferential removal of aromatic groups. Possibly some hydroxylated aromatic rings are sites of attack. The principal products, black acids, from oxygen and NaOCl oxidations in water at pH 13 have similar compositions.

Cleavages of Asphaltols

Results of cleavages of asphaltols, probably at ether links, are summarized in Figures 1 and 2. Each half of each table starts from the center with asphaltol with slightly different \bar{M}_n . In general, reactions were run under nitrogen, and at room temperature except as noted. Products were sometimes separated by solubility but always washed free of reagents and solvents and dried in an Abderhalden drier at <0.001 torr, usually at 140°C in Figure 1, usually at 76°C in Figure 2. (The only need for 140° drying seems to be with samples that contain pyridine or amines and have not been acid-washed.) \bar{M}_n s were determined by VPO in pyridine, in which all products were soluble, at concentrations of 0.5 to 3g/L. Keys to abbreviations and

arrangement of data are given in Figure 2. Thus, molecular weights of products are in the middle of each second line of each block of data.

Experiments in the upper left quarter of Figure 1 show that eight extractions of asphaltol with 5% KOH at room temperature resulted in solution and recovery of 9% of soluble carbon. 23% of the original C was lost, at least partly as water-soluble and/or volatile products. Molecular weight reductions without heating parallel those at 78°.2

Reactions of asphaltol with benzylamine (lower left quarter in Figure 1), and then drowning the reaction in ether or methanol, resulted in part of the asphaltol becoming soluble in these solvents and a decrease in \bar{M}_n of about one-half. Treatment of the ether-insoluble product with alcoholic KOH resulted in fractionation of the product but not further degradation. The butylamine-methanol combination appears to behave similarly.

Pyridine hydroiodide in pyridine at room temperature decreases the \bar{M}_n of asphaltol to one-half to one-third of the original (upper right in Figure 1). This experiment was run on the premise that pyridine hydroiodide would be an acid in pyridine, which is an excellent solvent for asphaltol. However, methyl iodide was nearly as effective as HI. Asphaltol was treated with methyl iodide at room temperature in the hope of making sulfonium as well as pyridinium salts. The product was then heated to 140° at reduced pressure in the expectation of splitting out methyl iodide from pyridinium salts (without net coal bond cleavage) and conversion of the original sulfides to methyl sulfides and coal alkyl iodides, with net cleavage of sulfide bonds. However, the reduction in \bar{M}_n from 1250 to 660 is surprisingly high, since the 1.7% S content corresponds to only 0.66 S/asphaltol molecule, of which most is expected to be in heterocyclic aromatic rings. A somewhat greater reduction in \bar{M}_n is reported for a duplicate experiment in Figure 2. It is therefore possible that I^- alone may be able to cleave ether links, a conclusion to be supported in discussion of Figure 2. Thus, abilities of Me_3SiI^4 and of hexamethyldisilazane plus ME_3SiCl (the latter intended for trimethylsilylation⁵) to cleave asphaltols may be due as much or more to halide ions generated as to the original reagent.

We tried sodium in liquid ammonia as an ether-cleaving reagent, but found that addition of sodium in liquid ammonia to a cold solution of asphaltol in butylamine gave better control, less reduction of the asphaltol, and a decrease in \bar{M}_n by nearly 50%. Treatment of this product with pyridine hydroiodide (right center of Figure 1) then gave further reduction in molecular weight. However, our data suggest that combination of the sodium and HI reactions gave no more cleavage than HI alone.

Figure 2 summarizes cleavage reactions of two other asphaltols with HI (check of Figure 1 experiment), HBr, toluene sulfonic acid, and some metal salts, all (except the MeI experiment) in pyridine solution. The other acids, even at 50°, are not as effective as HI at room temperature, but zinc bromide, and especially zinc chloride and $LiI \cdot H_2O$,⁶ have given more molecular weight reduction than any of the acids. However, all of these reactions have apparently resulted in incorporation of pyridine in the products, as shown by the high recoveries and high nitrogen contents. Some products also lose weight slowly and persistently on heating at 140° in vacuo. A possible explanation is that cleavage of an aryl alkyl ether by metal halide gives metal phenolate and alkyl halide; some of the latter then reacts with pyridine solvent to give unstable quaternary pyridinium salts. However, the remarkable reactivity of these reagents at low temperatures may be associated with the use of pyridine as solvent.

Conclusions

This progress report shows that asphaltol from Illinois No. 6 coal can be extensively degraded at or near room temperature by several acidic and basic reagents and by some oxidizing and reducing agents, with good to excellent recovery of original

carbon. These agents appear to attack ether links, or maybe aromatic rings in oxidations at pH 13, but as yet we know of no precedent for reactions of aliphatic amines or alcoholic KOH with ethers at these temperatures. To determine the proportions of various kinds of breakable single bonds in Illinois No. 6 coal, we plan to carry out further degradations on asphaltol by combinations of reagents, and then extend the most promising of these reactions to extracted coal. We expect that this kind of information will provide the basis for new and economical approaches to coal liquefaction, which will employ much milder conditions and much less expensive processes and plants.

Acknowledgement

Most of the research described here was supported by the U.S. Department of Energy under Contract No. ET-78-C-01-3293.

References

- (1) Present address, Department of Chemistry, Eastern Illinois University, Charleston, IL, 61920.
- (2) J. G. Huntington, F. R. Mayo, and N. A. Kirshen, *Fuel*, 58, 24 (1979).
- (3) F. R. Mayo and N. A. Kirshen, *Fuel*, in press.
- (4) M. E. Jung and M. A. Lyster, *J. Org. Chem.*, 42, 3761 (1977).
- (5) S. Friedman, M. L. Kaufman, W. A. Steiner, and I. Wender, *Fuel*, 40, 33 (1961).
- (6) I. T. Harrison, *Chem. Communications*, 1969, 616.

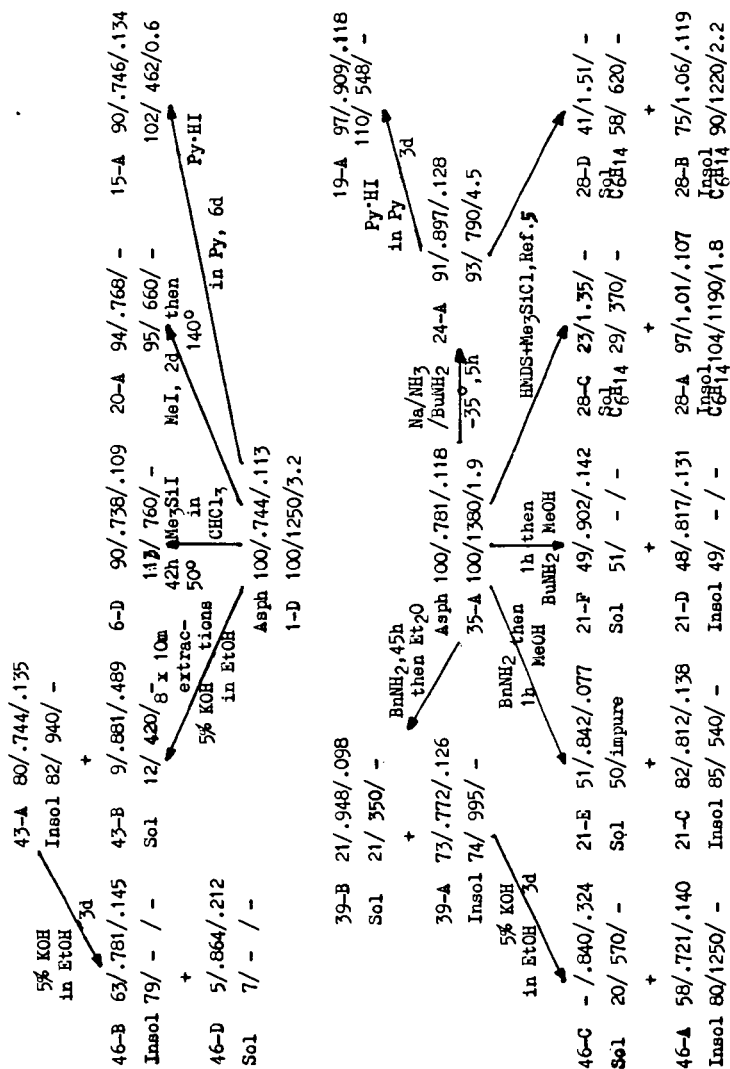
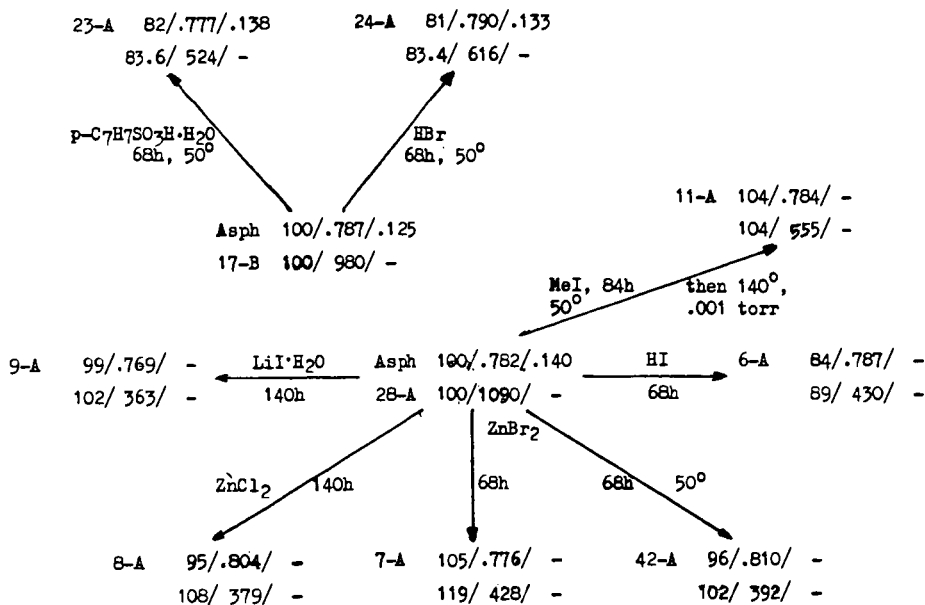


Figure 1. Cleavages of asphaltols, at room temperature, except as noted.
Key and abbreviations are in Figure 2.



Key to arrangement of data:

Sample Atom % C/ H/C / O/C
 ↑
 Yield
 ↓
 No. Wt. % / \bar{M}_n /eq.OH/mole

Abbreviations:

As = asphaltol
 Bn = benzyl
 Bu, Et, Me = n-butyl, ethyl, methyl
 HMDS = hexmethyldisilazane
 d, h, m = days, hours, minutes

Figure 2. Cleavages of asphaltols in pyridine solution (except with MeI) and at room temperature (except as noted otherwise).